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Strain Splitting of the Gamma(5) and Gamma(6) Free Excitons in ZnO

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High-quality ZnO crystals have been grown by vapor-phase techniques and by the hydrothermal method. Depending on the surface preparation technique, some hydrothermally grown crystals contain strain. These strains result in energy shifts of the free excitons as well as relaxation of the selection rules. The Γ_6 unallowed exciton is observed in these samples without the application of a magnetic field. The Γ_6 exciton is also observed to split in a strain field, consistent with the Γ_9 symmetry for the top valence band in ZnO. The Γ_5 and Γ_6 excitons have been observed to split in the strain field. The splitting is believed due to combined strain and electron–hole spin exchange. © *1999 American Institute of Physics.* [S0021-8979(99)08022-6]

INTRODUCTION

High-quality ZnO crystals have been grown by vapor-phase[1] and hydrothermal methods.[2] We have found that, depending on the surface preparation technique, some hydrothermally grown crystals contain strain. These strains result in energy shifts of the free excitons as well as relaxation of the selection rules. In the standard wurtzite structure, the conduction band has Γ_7 symmetry while the top valence band has Γ_9 symmetry, and the next two lower valence bands have Γ_7 symmetry. Exciton symmetries associated with optical transitions between these bands are as follows:

$$\Gamma_7 \times \Gamma_9 \rightarrow \Gamma_5 + \Gamma_6,$$

$$\Gamma_7 \times \Gamma_7 \rightarrow \Gamma_5 + \Gamma_1 + \Gamma_2.$$

The fundamental exciton spectra in ZnO crystals were first investigated by Thomas.[3] From reflection measurements he identified three exciton series, one associated with each of the three valence bands. Analyzing polarization measurements of both reflection and absorption spectra he concluded that states from the first and third valence bands were mixed and that the symmetries of the two top valence bands were reversed with respect to the usual ordering in the wurtzite structure, thus assigning Γ_7 symmetry to the top valence band.

The Γ_5 and Γ_1 excitons are allowed while the Γ_6 and Γ_2 excitons are forbidden; also, the Γ_5 and Γ_6 excitons are doubly degenerate while the Γ_1 and Γ_2 excitons are singly degenerate. In strain-free crystals, the selection rules are relaxed in the presence of an applied magnetic field, allowing the forbidden excitons to be observed. In hydrothermally grown crystals containing strain we have observed a forbidden exciton in appropriate polarizations without an applied magnetic field. Also, in grating second order (which gives higher resolution), this exciton shows line splitting due to strain.

The splitting of exciton lines in wurtzite crystals when exposed to an applied stress was first reported by Koda and Langer.[4] In the case of wurtzite crystals, all of the orbital degeneracies of the valence band are lifted by the trigonal crystal-field and spin-orbit interactions. The above phenomena could not be explained by the one-electron-band scheme and deformation-potential theory. A theoretical interpretation was provided by Akimoto and Hasegawa.[5] They found that the combined effects of stress and the electron–hole exchange interaction in a quasicubic model were able to predict the splitting and polarization pattern of the free exciton. These investigations were extended to several materials by Langer *et al.*[6] Their investigations primarily involved reflection measurements; as a result, the individual excitons that make up the band were not resolved. In the analysis of Ref. 5 only the splitting of the Γ_5 exciton was treated. The Γ_6 and Γ_2 excitons were not considered since they are forbidden. In the current experiment, the excitons are being observed in emission and both the Γ_5 and a forbidden exciton are resolved. In the absence of a magnetic field, the forbidden exciton is only observed in samples containing in-grown strain. It would be expected that strain would relax selection rules since it changes the symmetry of the sample. Not only is the forbidden exciton observed in the presence of strain but it also splits. In Ref. 5 it was pointed out that it is the combined effects of strain and exchange coupling which

causes line splitting. If either one is zero, the line splitting is also zero. This allows the identification of the unallowed exciton as a Γ_6 exciton rather than a Γ_2 exciton since the latter is a singlet and would not split. These data are, therefore, consistent with the top valence band in ZnO having Γ_9 symmetry. The individual excitons that make up the band have been observed to split in the strain field. The splitting is thought to result from the combined strain and electron–hole exchange interaction.

EXPERIMENTAL DETAILS

One of the ZnO samples was grown by a seeded physical vapor transport method. The ''*c*'' axis of the crystal is normal to the growing surface. Temperature-dependent Hall-effect measurements yielded a hydrogenic (60 meV) donor concentration N_D of $1\times10^{17}\,\mathrm{cm}^{-3}$, and a total acceptor concentration N_A of $2\times10^{15}\,\mathrm{cm}^{-3}$. The two other samples were hydrothermally grown in an autoclave equipped with a free-standing sealed platinum liner in which the ZnO nutrient material, mineralizer, and seed plate were contained. The seeds were (0001) plates of ZnO from previous hydrothermal growth runs. At the growth temperature, the nutrient zone was at 355 °C with a temperature gradient of 10 °C, declining to the seed plate. The Fermi level of this sample was controlled by a deeper donor (340 meV), and had $N_D=7\times10^{15}\,\mathrm{cm}^{-3}$ and $N_A=1\times10^{15}\,\mathrm{cm}^{-3}$. Different surface treatments were used to prepare the hydrothermal crystals: a mechanical polish provided by a commercial service, and a chemomechanical polish performed by Eagle Picher Corporation. Other than surface treatment, the preparation method of the two hydrothermal crystals was essentially the same. Photoluminescence (PL) spectral measurements were made at 2 K with the sample immersed in liquid He. PL excitation was achieved with the 3250 Å line of a He–Cd laser. The PL spectra were analyzed by means of a high-resolution 4-m grating spectrometer equipped with an RCAC31034A photomulitiplier tube for detection.

EXPERIMENTAL RESULTS

The individual excitons associated with the *A* band (top valance band in ZnO) have been previously observed in strain-free crystals.[7] These are the Γ_5 and Γ_6 excitons and are resolved in emission experiments, the Γ_6 exciton being observed only in an applied magnetic field. In Fig. 1(a), the emission spectra are shown superimposed on the reflection spectrum in the orientation $E\perp c$, for a ZnO crystal grown from the vapor phase. In zero-magnetic field only the Γ_5 exciton is observed, while with the application of a magnetic field $E\perp c$, the Γ_6 exciton is clearly seen. In Fig. 1(b), similar spectra for a hydrothermally grown ZnO crystal without strain are shown. The spectra are very similar to those observed for crystals grown from the vapor phase. This confirms that high-quality ZnO crystals can be grown by both vapor-phase and hydrothermal techniques. In Fig. 2, the emission spectra are shown for a hydrothermally grown ZnO crystal whose near-surface region does contain strain. In this crystal, the emission transitions are shifted to lower energies by approximately 3 meV; also, the Γ_6 exciton is observed in zero-magnetic field. With the polarizer oriented perpendicular to the *c* axis of the crystal ($E\perp c$), the Γ_6 exciton is not observed. When the polarizer is oriented $E\|c$, the Γ_6 exciton is clearly seen. In this case, the selection rules are relaxed by the strain. The orientation of the strain is not known; it is, however, believed to be preferentially in the direction of the ''*c*'' axis. Here, the effect of the strain is similar to that of the magnetic field in strain-free crystals, Fig. 1.

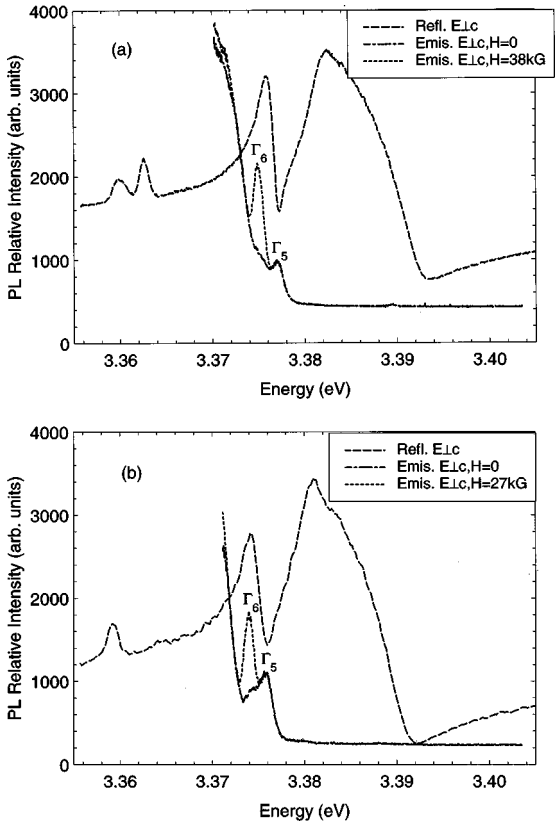

FIG. 1. (a) Superimposed reflection and emission spectra from a ZnO crystal grown from the vapor phase. (b) Superimposed reflection and emission spectra from a strain-free ZnO crystal grown hydrothermally.

When viewing the Γ_5 and Γ_6 excitons in grating second order, a well-resolved splitting of the Γ_6 exciton is observed, solid line, Fig. 3. The emission line from the Γ_5 exciton is broadened, suggesting a splitting which is not resolved.

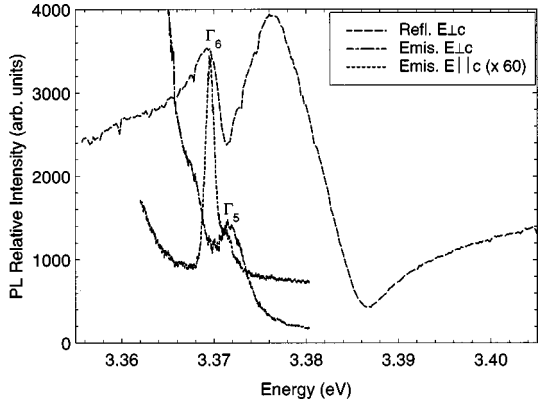

FIG. 2. Superimposed reflection and emission spectra from a hydrothermally grown ZnO crystal containing strain.

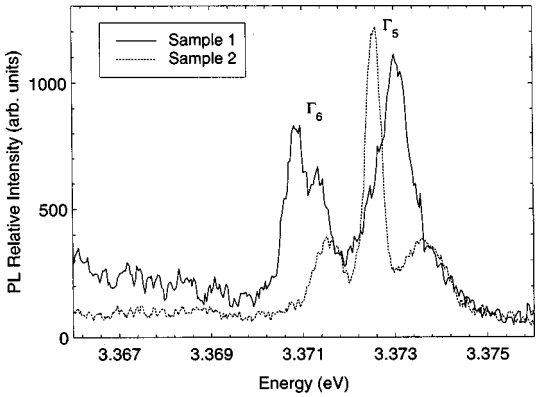

FIG. 3. Second-order emission spectra in the Γ_5, Γ_6 free-exciton region from two different hydrothermally grown ZnO crystals, both containing strain.

Here, the polarizer is oriented $E\|c$. The emission spectrum from a second hydrothermally grown ZnO crystal is shown as the dashed line in Fig. 3. The superimposed spectra from samples 1 and 2 show a small shift in the energy of the Γ_5 and Γ_6 excitons as well as a three-line splitting for sample 2. The center line is believed to be composed of components of both the Γ_5 and Γ_6 excitons. The orientation of the polarizer is again $E\|c$. The polarized spectra for sample 2 are shown in Fig. 4. The solid line shows the unpolarized spectrum, and the dashed line shows the spectrum polarized in the orientation $E\perp c$. In this orientation, the Γ_6 exciton is not observed while the Γ_5 exciton is split; one component of the latter is coincident with the center component of the unpolarized spectrum, and the other component is at essentially the same

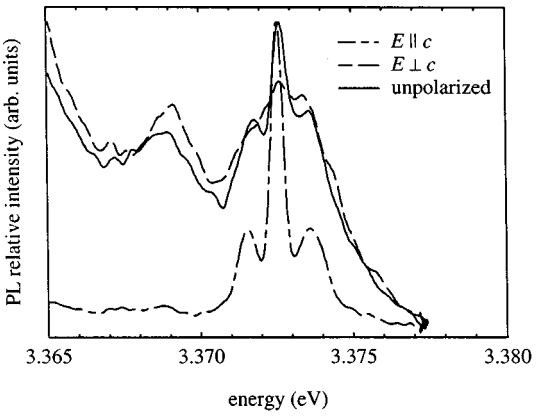

FIG. 4. Polarization spectra from sample 2.

energy as the high-energy component of the unpolarized spectrum. The dot-dashed curve shows the spectrum polarized in the orientation $E\|c$. In this orientation, the low-energy component of the Γ_6 exciton is observed in the same position as the low-energy component of the unpolarized spectra. It is believed that the magnitude of the strain in this sample is causing the high-energy component of the Γ_6 exciton to overlap the low-energy component of the Γ_5 exciton. From Fig. 3, it is probable that an appropriate increase in strain would result in the overlap of these two components. The intensity of the unpolarized spectrum is a factor of 3 greater than the intensity of the spectrum polarized with $E\perp c$, and is 20 times greater than that polarized with $E\|c$. This is not surprising since the Γ_5 exciton is only allowed for $E\perp c$, and the Γ_6 exciton becomes allowed due to the presence of strain. The relevant polarization is expected to be in the direction of the strain, suggesting that the strain is preferentially oriented $E\|c$, but the exact orientation is not known.

In conclusion, we have observed strain that relaxes the selection rules in ZnO, permitting the unallowed Γ_6 exciton to be observed in the absence of an applied magnetic field. We have also observed the splitting of the Γ_6 exciton resulting from combined strain and electron–hole spin exchange. This reflects the Γ_9 symmetry of the top valence band in ZnO.

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